A New Approach To The Evaluation Of The S-Matrix In Atom-Diatom Quantum Reactive Scattering Theory

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Abstract

A new approach is described to the evaluation of the $\boldsymbol{S}$-matrix in three-dimensional atom-diatom reactive quantum scattering theory. The theory is developed based on natural collision coordinates where progress along the reaction coordinate can be viewed as fulfilling the same role as time in a time-dependent formulation. By writing the full wavefunction in coupled-channel form it is proved that the $3D$ quantum reactive scattering problem can be treated in the same way as an inelastic single-arrangement problem. In particularly, two types of coupled-channel representations, which are reduced to two different systems of coupled first order ordinary differential equations describing the inelastic scattering, are used. The first system of coupled differential equations is constructed on a set of points (grid) of the coordinate reaction curve after solution of many $1D$ Schrödinger problems in the directions normal to the reaction coordinate. The second expression for inelastic scattering is found using exactly solvable nonstationary $1D$ Schrödinger equation (etalon equation method), which is introduced for describing the localization properties of the full wavefunction along the curve of coordinate reaction. In this case we avoid a large amount of computation involved in solving the $1D$ Schrödinger problem along the reaction coordinate by using a slightly difficult initial conditions for the inelastic scattering equations. In both cases by solving the system of coupled first order ordinary differential equations, the full wavefunction and all $\boldsymbol{S}$-matrix elements are obtained simultaneously without further calculations. Our analysis shows that the methods we have developed constitute the simplest algorithms for computing the reactive scattering $\boldsymbol{S}$-matrices.

Keywords: Quantum Scattering, Natural Collision Coordinate, Etalon Equation Method, $\boldsymbol{S}$-matrix Elements, Coupled-Channel Differential Equations, Quantum Theory of Chemical Reactions

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I. INTRODUCTION

Accurate quantum dynamics approaches have made an immense impact on the theory of elementary atom-molecule collisions [1, 2, 3]. Recent advances in accurate quantum mechanical calculations on simple few atom systems have demonstrated the possibility of obtaining detailed information concerning chemical reactions from first principles [4, 5, 6]. Tremendous progress has occurred in developing and applying both time-independent and time-dependent quantum dynamics approaches the last few years.

At present there are three common approaches used in the quantum reactive scattering field:

1. The hyperspherical coordinate methods [7, 8],

2. The variational methods based on the simultaneous use of mass-scaled Jacobi coordinates in each of the chemical arrangements involved [9, 10, 11] and

3. Wavepacket methods [12, 13] (many references can be found in the review [14]).

Both time-dependent and time-independent approaches have been successfully applied to three- and four-atom reactions. For detailed information at low energy the time-independent hyperspherical coordinate approach has proven the most useful [4, 15]. The time-dependent wavepacket method has also proved to be very useful, particularly for photodissociation and laser-molecule interaction problems. To go beyond four-atom systems, the Multi-Configurational Time-Dependent Hartree method has been applied in full-dimensionality to calculate thermal rate constants for the H + CH_4 [16] and O + CH_4 [17] reactions.

Despite the successful applications to polyatomic systems mentioned above, general applications still appear to be extremely difficult. Quantum mechanics is nonlocal in character and numerical efforts to solve the Schrödinger equation increase exponentially with the number of degrees of freedom. State resolved accurate quantum dynamical calculations are presently limited to at most seven-dimensional problems [16]. Thus, the development of new conceptual approaches permitting improved computational algorithms for accurate quantum simulations is of great interest.

Earlier *natural collision coordinates* NCC allowing an analytical investigation of chemical reactivity in collinear collisions were introduced by Marcus [18] and further explored by Light [19, 20]. Light and coworkers [21, 22] generalized the NCC approach to three-dimensional
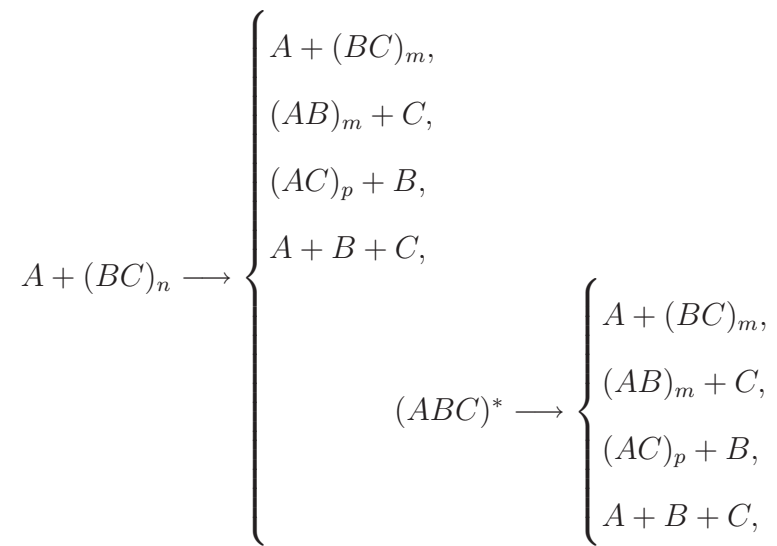
atom-diatom reactive scattering and on this basis they studied H + H$_2$ system and its isotopomers in $3D$ for total angular momentum $J = 0$ [23]. Related developments have been the formulation and later use of the reaction-path hamiltonian formalism by Miller, Handy and Adams [24] and the reaction path and reaction volume approaches advocated by Billing [25, 26, 27, 28].

Due to difficulties in applying the NCC approach, attention turned to other coordinate systems. Nevertheless, it seems to us that the primary idea of NCC, namely to simplify $3D$ quantum reactive scattering calculations, can be realized. Particularly, one of the authors has shown that for collinear three-body collisions, it is possible to constructed the $\boldsymbol{S}$-matrix exactly, in simple form using the approach [29, 30]. Seven reactive systems, N$_2$ + N, N$_2$ + O, O$_2$ + O, Li + FH, O$_2$ + N etc have been studied successfully within this framework [31].

The aim of the current article is to generalize our previous collinear NCC quantum scattering approach to a full three dimensional treatment.

II. QUANTUM MULTI-CHANNEL SCATTERING PROBLEM IN DIFFERENT COORDINATE SYSTEMS

The reactive scattering process in a three-body system can be described by the scheme:

$$
A + (BC)_n \longrightarrow
\begin{cases}
A + (BC)_m, \\
(AB)_m + C, \\
(AC)_p + B, \\
A + B + C, \\
\qquad (ABC)^* \longrightarrow
\begin{cases}
A + (BC)_m, \\
(AB)_m + C, \\
(AC)_p + B, \\
A + B + C,
\end{cases}
\end{cases}
$$

$$Sch. \ 1.$$

where A, B, and C are atoms, n and m, p characterize quantum numbers of diatomic states corresponding to initial (in) and final (out) scattering channels, $(ABC)^*$ denotes an activated
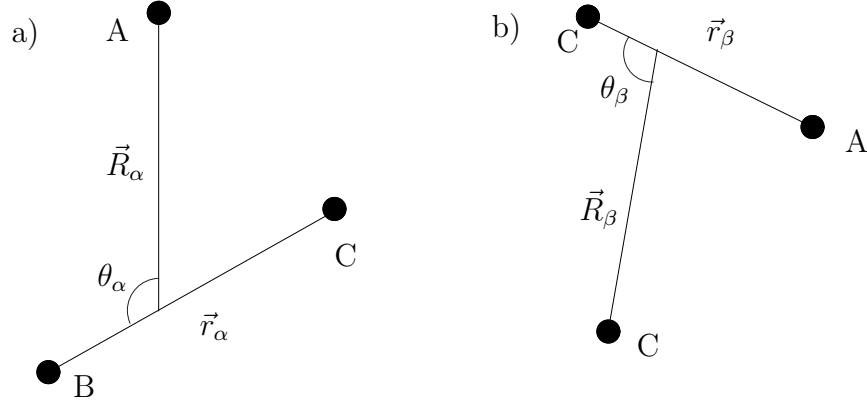
FIG. 1: *Jacobi coordinates for the reaction* $A+(BC)_n \to (AB)_m+C$ *corresponding to the reactant (a) and to the product (b) channels.*

complex which may or may not be present as an intermediary species.

A. The coordinate systems

We denote the masses of the particles by m_A, m_B and m_C and the coordinates of the particles are denoted by the column vectors $\mathbf{r_A}, \mathbf{r_B}$ and $\mathbf{r_C}$ describing their positions relative to an origin fixed in the laboratory system. The initial $9D$ problem can be reduced to a $6D$ one by elimination of the center-of-mass coordinates.

Below we consider the reaction $A + (BC)_n \to (ABC)^* \to (AB)_m + C$, i.e. there are two open arrangements.

For this reaction reactant and product Jacobi coordinates are illustrated in Fig.1. The following equations define the Jacobi coordinates $\mathbf{R}_\alpha$ and $\mathbf{r}_\alpha$ (note that index α corresponds to (in) or reactant asymptotic channel):

$$\mathbf{R}_\alpha = \mathbf{r}_A - \frac{m_B\mathbf{r_B} + m_C\mathbf{r_C}}{m_B + m_C}, \qquad \mathbf{r}_\alpha = \mathbf{r_C} - \mathbf{r_B},$$

$$\left(\mathbf{R}_\alpha \equiv \mathbf{R}_\alpha(R_x, R_y, R_z), \ \ \mathbf{r}_\alpha \equiv \mathbf{r}_\alpha(r_x, r_y, r_z)\right). \tag{1}$$

We now apply the Delves-Smith scale transformation [7, 11, 32] to obtain the new scaled coordinates $\mathbf{q_0}$ and $\mathbf{q_1}$;

$$\mathbf{q_0} \equiv \mathbf{q_{0\alpha}} = \lambda\,\mathbf{R}_\alpha, \qquad \mathbf{q_1} \equiv \mathbf{q_{1\alpha}} = \lambda^{-1}\,\mathbf{r}_\alpha. \tag{2}$$

where

$$\lambda = \left[\frac{m_A}{\mu}\left(1 - \frac{m_A}{M}\right)\right]^{1/2}, \qquad \mu = \left[\frac{m_A m_B m_C}{M}\right]^{1/2}, \qquad M = m_A + m_B + m_C. \qquad (3)$$

In these coordinates the Hamiltonian of a three-body system takes the following diagonal form:

$$H(\mathbf{q}; \mathbf{P_q}) = \frac{1}{2\mu}\mathbf{P}_{\mathbf{q}}^2 + V(q_0, q_1, \theta), \qquad (4)$$

where

$$\mathbf{q} = (\mathbf{q_0}, \mathbf{q_1}) = \{q_k\}, \quad k = 0, ..., 5; \quad \{q_k\} = (q_0 = |\mathbf{q_0}|, \ q_1 = |\mathbf{q_1}|, \ q_2, \ q_3, \ q_4, \ q_5).$$

Note that here and in the following we omit the α channel index for simplicity. In Eq. (4) μ is the reduced mass defined in Eq. (3), $\mathbf{P_q}$ is the moment vector conjugate to $\mathbf{q}$, in the body-fixed system and θ is the angle between vectors $\mathbf{q_0}$ and $\mathbf{q_1}$ (see FIG. 1 and FIG. 2). An alternative coordinate system (q_0, q_1, q_2) is illustrated in FIG. 2. Either of the coordinate systems (q_0, q_1, q_2) and (q_0, q_1, θ) can be used to describe the motion of body-fixed system in the plane of the vectors $(\mathbf{q_0}, \mathbf{q_1})$ and they will be called intrinsic coordinates. The interaction potential between all atoms depends only on the intrinsic coordinates.

The coordinates (q_3, q_4, q_5) are taken to be the Euler angles $\Omega(\equiv \zeta_1, \zeta_2, \zeta_3)$, which orient the three-body system in the space-fixed frame (see for example refs. [13], [33] and [34]).

The optimal coordinate systems for reactants and products are different [9, 35]. This fact creates certain mathematical and computational complexities in the investigation of the reactive scattering problem. One way to proceed is to turn to a special type of curvilinear coordinates which continuously leads from reactant channel to product channel. The possibility of introducing the coordinate system which is simultaneously suitable for description of (in) and (out) asymptotic states was first time discussed in the work [36]. At last corrected version for collinear collision was presented in the work [18] and named *natural collision coordinate* (NCC) system.

In order to define the NCC appropriately, we connect the (in) and (out) asymptotic channels by a smooth curve $\Im_{if}$. The curve depends on two parameters, one of which can be chosen arbitrary and the other is system dependent. As progress along the curve represent the passage from reactant to product during this it will be called *reaction coordinate* [18, 19].
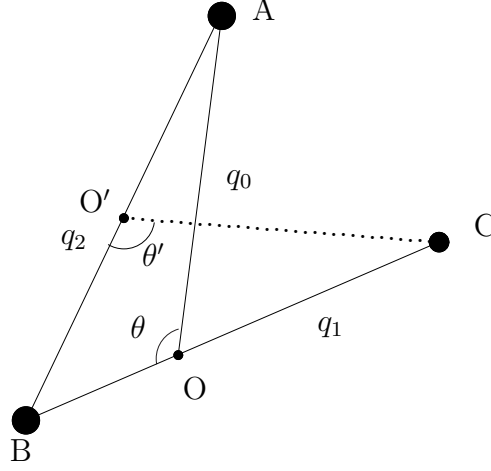
FIG. 2: *The three-body system in mass-scaled Jacobi coordinates. The coordinate q_0 shows the distance between particle A and the center of mass (BC) pair O, the distance between particles B and C is q_1 and q_2 correspondingly between A and C, θ is a Jacobi scattering angle. The point O' is a center of mass diatom (AB) and θ' is correspondingly Jacobi scattering angle which is used in (out) channel.*

The curve $\Im_{if}$, which connects (in) and (out) asymptotic channels can be determined in the plane $(q_0, q_1, \theta = 0)$, by simple formula:

$$q_0^c = \frac{a}{q_1^c - q_{eq}^-} + b\left(q_1^c - q_{eq}^-\right) + q_{eq}^+, \qquad q_{eq}^- < q_1^c < +\infty, \qquad (5)$$

where a and b are constants.

Note that the collinear collision configuration $A+(BC)$ describes on the plane $(q_0, q_1, \theta = 0)$ while the collinear collision $A+(CB)$ describes on the plane $(q_0, q_1, \theta = \pi)$. The motivation of choice of curve $\Im_{if}$ for later definition of $3D$ NCC system is given in the Appendix A. In Eq. (5) q_{eq}^- and q_{eq}^+ are mass-scaled equilibrium bond lengths of molecules in the (in) and (out) channels correspondingly. Note that a is an arbitrary constant, which is usually chosen to make the curve pass close to the saddle point of the reaction. The constant b depends on the mass of particles and is given by expression $b = cot\varphi = \left[m_A m_C / m_B M\right]^{1/2}$. The superscript c over q_0 and q_1 underlines the fact that the point (q_0^c, q_1^c) lies on the curve.

The limit $q_1^c \to q_{eq}^-$, $q_0^c \to \infty$ corresponds to the reactant region or (in) channel while the limit $q_1^c \to \infty$, $q_0^c \to \infty$ on the curve $\Im_{if}$ corresponds to the product region or (out) channel, where $q_0^c = bq_1^c + q_{eq}^+$. It is easy to show that the mass-scaled dis-

tance q_2 between A and B particles connected with the curve $\Im_{if}$ is described by expression $q_2^c = q_2\big|_{\Im_{if}} = \sqrt{(q_0^c)^2 - 2bq_0^c q_1^c \cos\theta + b^2(q_1^c)^2}$, which in the (in) channel is equal $\left(q_2^c - q_0^c\right)\big|_{q_1^c \to q_{eq}^-} = -bq_{eq}^- \cos\theta$. In other words it is denote that in the (in) channel curve $\Im_{if}$ is coming to the equilibrium distance q_{eq}^- of (BC) diatom. In the (out) channel the curve $\Im_{if}$ approaches the equilibrium distance q_{eq}^+ of diatom (AB) (see Appendix B). Note that the Jacobi scattering angle θ which defined in the reactant (or (in)) coordinates system in the product (or (out)) channel obviously must be limited to 0 inasmuch as the two sides $\overline{BO} = bq_1$ and $\overline{OA} = q_0$ of $\widehat{ABO}$ triangle are limited to infinity while the third side is limited to finite quantity $\overline{AB} = q_2 \to q_{eq}^+$. Remaind that it doesn't mean that the rotation of new-formed diatom (AB) stops. The rotation of diatom (AB) is described by angle θ' (see FIG. 2) which in the reactant region is limited to 0 but beginning from strong interaction region up to (out) asymptotic channel obviously can have any value.

The coordinate u describes the translational motion of three-body system between reactant and product channels and is changed along the curve $\Im_{if}$ measured from an initial point u_0. It particularly can be determined by equation:

$$u = u_0 - \frac{a}{q_1^c - q_{eq}^-} + b(q_1^c - q_{eq}^-). \tag{6}$$

The signed distance from the curve $\Im_{if}$ in the plane $(q_0, q_1, \theta = 0)$ is given by v. We can organize the one-to-one mapping between coordinate systems (q_0, q_1, θ) and (u, v, θ) in only some subspace of internal 3D configuration space. It should be emphasized that above mentioned subspace must include a part of 3D space, in which the probability current of reactive scattering process is localized. This condition can be fulfilled if the coordinate reaction curve $\Im_{if}$ is correctly determined for a configuration of reactive collision with the minimal energy surface (see FIG. 3). It is obvious that in this case the condition of one-to-one mapping between coordinate systems for any configuration of reactive collision can be automatically satisfied.

After satisfying aforementioned condition it is easy to write transformations between set of coordinates (q_0, q_1) and (u, v) [37]:

$$q_0(u, v) = q_0^c(u) - v \sin\phi(u),$$
$$q_1(u, v) = q_1^c(u) + v \cos\phi(u), \tag{7}$$

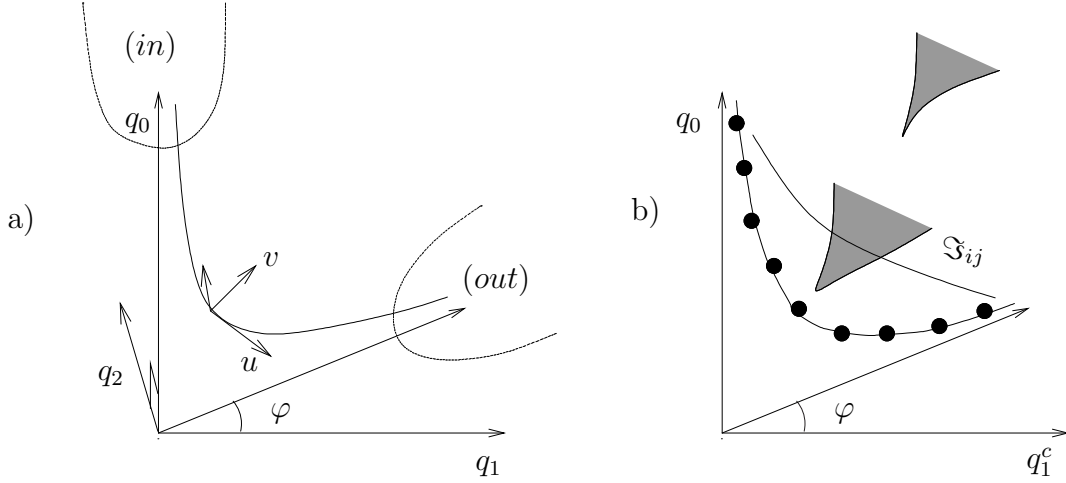where the angle $\phi(u)$ is determined from the requirement that the coordinate system (u, v)

FIG. 3: a) *Intrinsic 3D Jacobi and natural collision coordinate (NCC) systems. The angle φ is defined in the text. b) The reaction path (cycled curve) is passing through the minimums of potential energy while the reaction coordinate $\Im_{if}$ can be an arbitrary smooth curve connecting (in) and (out) asymptotic channels. The lower shaded area is self-crossing region for NCC system associated to the reaction path curve while the upper one self-crossing region for NCC system is associated to the curve $\Im_{if}$.*

should be orthogonal (see Appendix C):

$$\left.\frac{dq_0^c}{dq_1^c}\right|_{(u,v=0)} = \cot\phi(u), \qquad \lim_{u\to+\infty}\cot\phi(u) = \cot\varphi. \tag{8}$$

In the NCC system the motions of the body system are locally factorized into translational $\left(u,\text{ infinite extension}\right)$, vibrational $\left(v,\text{ finite}\right)$ and intrinsic rotational $\left(\theta,\text{ finite}\right)$ motions. Note that the coordinate u is perpendicular to the curve v and independent from the angle θ. These properties ensure that the full wavefunction can be conditionally (locally) factorized.

So, we defined NCC system for investigation of $3D$ reactive quantum scattering which for using has only one limitation related with the region of self-crossing of coordinate lines. In other words it is necessary to choose the reaction coordinate $\Im_{if}$ in such a way in order to the probability current of quantum reactive scattering process in the region of self-crossing of coordinate line was absent.

III. QUANTUM REACTIVE SCATTERING IN THE NCC SYSTEM

A. Equation of motion of the three-body system

The overall stationary wavefunction of three-body system can be written as:

$$\Psi^{JM}(q_0, q_1, \theta, \Omega) = \frac{1}{q_0 q_1} \sum_K \overline{\Phi}^J_K(q_0, q_1, \theta) D^J_{KM}(\Omega), \tag{9}$$

where J is the total angular momentum, M and K are its space-fixed and body-fixed z-components respectively. The summation over K ranges from $-J$ to $+J$ in unit steps and D^J_{KM} is the Wigner D-matrix [33, 34].

After separation of the external rotations, the action of the hamiltonian on the wavefunction is given by the formula [13, 20]:

$$
\begin{aligned}
\hat{H}\overline{\Phi}^J_K(q_0, q_1, \theta) &= -\frac{\hbar^2}{2\mu}\left\{ \frac{\partial^2}{\partial q_0^2} + \frac{\partial^2}{\partial q_1^2} \right\} \overline{\Phi}^J_K(q_0, q_1, \theta) \\
&\quad - \frac{\hbar^2}{2\mu}\left(\frac{q_0^2 + q_1^2}{q_0^2 q_1^2} \right)\left\{ \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} - \frac{K^2}{\sin^2\theta} \right\} \overline{\Phi}^J_K(q_0, q_1, \theta) \\
&\quad + V(R, r, \theta)\overline{\Phi}^J_K(q_0, q_1, \theta) + \frac{\hbar^2}{2\mu q_0^2}\left(J(J+1) - 2K^2 \right) \overline{\Phi}^J_K(q_0, q_1, \theta) \\
&\quad - \frac{\hbar^2}{2\mu q_0^2} c^+_{JK}\left\{ \frac{\partial}{\partial\theta} - (K+1)\cot\theta \right\} \overline{\Phi}^J_{(K+1)}(q_0, q_1, \theta) \\
&\quad + \frac{\hbar^2}{2\mu q_0^2} c^-_{JK}\left\{ \frac{\partial}{\partial\theta} + (K-1)\cot\theta \right\} \overline{\Phi}^J_{(K-1)}(q_0, q_1, \theta) \\
&= E\,\overline{\Phi}^J_K(q_0, q_1, \theta), \tag{10}
\end{aligned}
$$

where

$$c^\pm_{JK} = \left[J(J+1) - K(K\pm1) \right]^{1/2}. \tag{11}$$

After the coordinate transformation $(q_0, q_1, \theta) \rightarrow (u, v, \theta)$ in equation (10) we find:

$$
\begin{aligned}
\hat{H}\overline{\Phi}^J_K(u, v, \theta) &= -\frac{\hbar^2}{2\mu}\frac{1}{\eta}\left\{ \frac{\partial}{\partial u}\frac{1}{\eta}\frac{\partial}{\partial u} + \frac{\partial}{\partial v}\eta\frac{\partial}{\partial v} \right\} \overline{\Phi}^J_K(u, v, \theta) - \frac{\hbar^2}{2\mu}\frac{1}{q^2(u, v)} \times \\
&\quad \times \left\{ \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} - \frac{K^2}{\sin^2\theta} \right\} \overline{\Phi}^J_K(u, v, \theta) + U(u, v, \theta)\overline{\Phi}^J_K(u, v, \theta) \\
&\quad + E_{JK}\overline{\Phi}^J_K(u, v, \theta) + \frac{\hbar^2}{2\mu}\left\{ H^+_{JK}\overline{\Phi}^J_{(K+1)}(u, v, \theta) + H^-_{JK}\overline{\Phi}^J_{(K-1)}(u, v, \theta) \right\} \\
&= E\,\overline{\Phi}^J_K(u, v, \theta), \tag{12}
\end{aligned}
$$

where

$$E_{JK}(u,v) = \frac{\hbar^2}{2\mu q_0^2(u,v)}\Big(J(J+1) - 2K^2\Big), \quad H_{JK}^{\pm} = \frac{c_{JK}^{\pm}}{q_0^2(u,v)}\left\{\mp\frac{\partial}{\partial\theta} + (K\pm1)\cot\theta\right\},$$

$$q^2(u,v) = \frac{q_0^2(u,v)q_1^2(u,v)}{q_0^2(u,v) + q_1^2(u,v)}, \quad V(R,r,\theta) \equiv U(u,v,\theta), \quad \overline{\Phi}_K^J(q_0,q_1,\theta) \equiv \overline{\Phi}_K^J(u,v,\theta). \quad (13)$$

In expression (12) the Lamé coefficient $\eta(u,v)$ has a form (Appendix C):

$$\eta(u,v) = \big[1 + K(u)v\big]\frac{ds}{du}, \tag{14}$$

where $K(u)$ is described curvature of the reaction coordinate $\Im_{ij}$ in the continues point u, correspondingly s the length along the $\Im_{ij}$:

$$K(u) = \frac{2a}{\left(q_1^c - q_{eq}^-\right)^3}\left\{1 + \left[b - a/\left(q_1^c - q_{eq}^-\right)^2\right]^2\right\}^{-3/2}, \tag{15}$$

and

$$\frac{ds}{du} = \left\{1 + \left[b - a/\left(q_1^c - q_{eq}^-\right)^2\right]^2\right\}^{1/2}\left\{b + a/\left(q_1^c - q_{eq}^-\right)^2\right\}^{-1}. \tag{16}$$

Finally we transform Eq. (12) by setting $\overline{\Phi}_K^J(u,v,\theta) = \eta^{-1/2}\Phi_K^J(u,v,\theta)$, whereby we obtain:

$$\left\{\left[\frac{\partial}{\partial u}\frac{1}{\eta^2}\frac{\partial}{\partial u} + \frac{\partial^2}{\partial v^2}\right] + \frac{1}{q^2(u,v)}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} - \frac{K^2}{\sin^2\theta}\right] + \frac{2\mu}{\hbar^2}\big[E - U(u,v,\theta) - \right.$$

$$\left. E_{JK}(u,v) - U_{eff}(u,v)\big]\right\}\Phi_K^J(u,v,\theta) + \left\{H_{JK}^+\Phi_{(K+1)}^J(u,v,\theta) + H_{JK}^-\Phi_{(K-1)}^J(u,v,\theta)\right\} = 0,$$

$$(17)$$

where the effective potential $U_{eff}(u,v)$ is defined by

$$U_{eff}(u,v) = \frac{1}{4\eta^2}\left(\frac{\partial\eta}{\partial v}\right)^2 - \frac{1}{2\eta^3}\frac{\partial^2\eta}{\partial u^2} + \frac{5}{4\eta^4}\left(\frac{\partial\eta}{\partial u}\right)^2. \tag{18}$$

Schrödinger equation (17) is in a form which is suitable for further investigation by the coupled channels method. This will be done in section III. C after the S-matrix has been defined in Section III. B.

B. Definition of S-matrix in term of reaction coordinate

In the standard scattering theory the main problem is the construction of the scattering S-matrix, holding the transition amplitudes. Let us discuss the exact representation for the S-matrix in terms of overlap between stationary wavefunctions (see for example [38, 39]). In the body-fixed NCC system we can write the following general formal expression:

$$\Phi_{njK}^{(+)J}(u_\alpha, v_\alpha, \theta_\alpha) = \sum_{n'j'K'} S_{n'j'K' \leftarrow njK}^J \, \Phi_{n'j'K'}^{(-)J}(u_\beta, v_\beta, \theta_\beta), \tag{19}$$

where $\Phi_{njK}^{(+)J}(u_\alpha, v_\alpha, \theta_\alpha)$ and $\Phi_{n'j'K'}^{(-)J}(u_\beta, v_\beta, \theta_\beta)$ are the total stationary wavefunctions in correspondingly NCC systems which are evaluating from some clear (in) and (out) asymptotic states, n and j are vibration and rotation quantum numbers, $S_{n'j'K' \leftarrow njK}^J$ are an complex matrix elements.

For the overall wavefunction $\Phi_{njK}^{(+)J}(u, v, \theta)$ we may enforce the following asymptotic behaviors and boundary conditions:

$$\Phi_{njK}^{(+)J}(u, v, \theta) \underset{u \to -\infty}{\sim} \Phi_{njK}^{(in)J}(u, v, \theta),$$

$$\Phi_{njK}^{(+)J}(u, v, \theta) \underset{u \to +\infty}{\sim} \sum_{n'j'K'} S_{njK \leftarrow n'j'K'}^J (E) \, \Phi_{n'j'K'}^{(out)J}(u, v, \theta),$$

$$\lim_{|v| \to \infty} \Phi_{njK}^{(+)J}(u, v, \theta) = \lim_{|v| \to \infty} \frac{\partial}{\partial v} \Phi_{njK}^{(+)J}(u, v, \theta) = 0. \tag{20}$$

where $\Phi_{njK}^{(in)J}(u, v, \theta)$ and $\Phi_{n'j'K'}^{(out)J}(u_\beta, v_\beta, \theta_\beta)$ are an asymptotic wavefunctions correspondingly in the (in) and (out) channels, $S_{njK \leftarrow n'j'K'}^J$ are a reactive S-matrix elements.

Similar conditions can be also written for wavefunction $\Phi_{njK}^{(-)J}(u, v, \theta)$. For later calculations it is important to define the behavior of the wavefunction $\Phi_{njK}^{(-)J}(u, v, \theta)$ in the (out) asymptotic channel:

$$\Phi_{njK}^{(-)J}(u_\beta, v_\beta, \theta_\beta) \underset{u \to +\infty}{\sim} \Phi_{njK}^{(out)J}(u_\beta, v_\beta, \theta_\beta). \tag{21}$$

Note that in (20) and (21) the functions $\Phi_{njK}^{(in)J}(u, v, \theta)$ and $\Phi_{njK}^{(out)J}(u_\beta, v_\beta, \theta_\beta)$ are described by expressions:

$$\Phi_{njK}^{(in)J}(u, v, \theta) = \frac{1}{\sqrt{2\pi}} \exp\left(-ip_{nj}^- u\right) \Pi_{n(j)}^{(in)}(v) \Theta_{jK}(\theta),$$

$$\Phi_{njK}^{(out)J}(u_\beta, v_\beta, \theta_\beta) = \frac{1}{\sqrt{2\pi}} \exp\left(ip_{nj}^+ u_\beta\right) \Pi_{n(j)}^{(out)}(v_\beta) \Theta_{jK}(\theta_\beta), \quad p_{nj}^\mp = \frac{1}{\hbar}\sqrt{2\mu\left(E - \epsilon_{n(j)}^\mp\right)}, \tag{22}$$

where $\epsilon^-_{n(j)}$ is the vibration-rotational energy of the initial state of the diatomic, $\epsilon^+_{n(j)}$ is vibration-rotational energy of the final state, $\Theta_{jK}(\theta)$ is a normalized associated Legendre polynomial [34], $\Pi^{(in)}_{n(j)}(v)$ is the vibrational wavefunction of the initial diatomic, which satisfies the following equation:

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dv^2} + U^{(in)}(v) + \frac{\hbar^2 j(j+1)}{2\mu v^2} \right] \Pi^{(in)}_{n(j)}(v) = \epsilon^-_{n(j)}\,\Pi^{(in)}_{n(j)}(v), \tag{23}$$

where $U^{(in)}(v)$ is bounding potential of diatom. Similar expression is valid for $\Pi^{(out)}_{n(j)}(v)$ after replacing $U^{(in)}(v) \to U^{(out)}(v)$ and $\epsilon^-_{n(j)} \to \epsilon^+_{n(j)}$.

The matching conditions between α and β full internal wavefunctions can be write in the following form (see for example [11, 40]):

$$\sum_{\bar{K}} D^J_{M\bar{K}}(\zeta_{1\alpha},\zeta_{2\alpha},\zeta_{3\alpha})\rho_\alpha^{-1/2}\Phi^{(\pm)J}_{nj\bar{K}}(u_\alpha,v_\alpha,\theta_\alpha) = \sum_{\bar{K}} D^J_{M\bar{K}}(\zeta_{1\beta},\zeta_{2\beta},\zeta_{3\beta})\rho_\beta^{-1/2}\Phi^{(\pm)J}_{nj\bar{K}}(u_\beta,v_\beta,\theta_\beta),$$

$$\rho_\varsigma(u_\varsigma,v_\varsigma) = \eta_\varsigma q_{0\varsigma}^2 q_{1\varsigma}^2, \qquad \varsigma = \{\alpha\,\beta\}, \tag{24}$$

The relation between the rotation functions in different body-fixed frames in (24) as well know may be represent by formula [11, 40, 41]:

$$D^J_{M\bar{K}}(\zeta_{1\beta},\zeta_{2\beta},\zeta_{3\beta}) = \sum_{K'} d^J_{MK'}(\vartheta)D^J_{\bar{K}K'}(\zeta_{1\alpha},\zeta_{2\alpha},\zeta_{3\alpha}). \tag{25}$$

Note that ϑ is the angle between vectors $\mathbf{q}_{0\alpha}$ and $\mathbf{q}_{0\beta}$, and may be described as a function of the internal coordinates using the relation:

$$\mathbf{q}_{0\alpha}\mathbf{q}_{0\beta} = q_{0\alpha}q_{0\beta}\cos\vartheta, \tag{26}$$

where ϑ-angle between α and β body-fixed reaction coordinates systems.

Using the expressions (24) and (25) it is easy to find the following equation of connection (Appendix D):

$$\Phi^{(\pm)J}_{nj K}(u_\alpha,v_\alpha,\theta_\alpha) = \sqrt{\frac{\rho_\alpha}{\rho_\beta}}\sum_{\bar{K}} d^J_{K\bar{K}}(\vartheta)\Phi^{(\pm)J}_{nj\bar{K}}(u_\beta,v_\beta,\theta_\beta) \tag{27}$$

Now taking into account that the overall wavefunction $\Phi^{(+)J}_{nj\bar{K}}(u_\beta,v_\beta,\theta_\beta)$ at the limit $u \to +\infty$ going to clear (out) asymptotic state (21) from equation (19) we can fined the following expression for scattering matrix (see Appendix D):

$$S^J_{n'j'K' \leftarrow njK}(E) = \lim_{u\to+\infty}\left\langle \Phi^{(+)J}_{njK}(u_\alpha,v_\alpha,\theta_\alpha)\Phi^{(out)J}_{n'j'K'}(u_\beta,v_\beta,\theta_\beta)\right\rangle_{v\theta},$$

$$\langle...\rangle_{v\theta} = \int_v \eta^{1/2}\,dv \int_\theta \sin\theta\,d\theta. \tag{28}$$

Putting the expression for $\Phi_{njK}^{(+)J}(u_\alpha, v_\alpha, \theta_\alpha)$ from (27) in the (28) we can find:

$$S_{n'j'K' \leftarrow njK}(E) = \sqrt{\frac{p_{n'j'}^+}{p_{nj}^-}} \lim_{u \to +\infty} \left\langle \Phi_{njK}^{(+)J}(u, v, \theta) \Phi_{n'j'K'}^{(out)J}(u, v, \theta) \right\rangle_{v\theta}. \qquad (29)$$

In the expression (29) $S_{n'j'K' \leftarrow njK}$ maybe interpreted as a general form for the reactive **S**-matrix elements. Evidently from definition of the **S**-matrix elements (29) the integration over coordinate u is absent, however it is easy to understand that in the (*out*) asymptotic region the full phase is cancelled out and thus $S_{n'j'K' \leftarrow njK}$ -matrix elements become independent from coordinate u.

Now the differential reactive state-to-state cross section may be simply constructed with the help of matrix elements $S_{n'j'K \leftarrow njK}^J(E)$ (see particularly works [1, 13, 42]):

$$\sigma_{n'j' \leftarrow nj}(E, \vartheta) = \frac{1}{2j+1} \sum_{KK'} \frac{1}{4p_{nj}^2} \left| \sum_J (2J+1) S_{n'j'K' \leftarrow njK}(E) \, d_{KK'}^J(\vartheta) \right|^2, \qquad (30)$$

where p_{nj} is the incoming wave vector.

The total integral reactive cross section for reaction from a particular initial state to all possible final states is then given by a summation over all total angular momenta which can contribute to the reaction:

$$\sigma_{all \leftarrow nj}^{tot} = \frac{\pi}{p_{nj}^2} \sum_J (2J+1) P_r^J(E), \qquad (31)$$

where

$$P_r^J(E) = \frac{1}{2j+1} \sum_{n'j'} \sum_{KK'} \left| S_{n'j'K' \leftarrow njK}(E) \right|^2. \qquad (32)$$

Recall that $P_r^J(E)$ total reaction probability for a particular value of the total angular momentum J.

So, we have obtained a new representation (29) for the scattering **S**-matrix, where the coordinate u, which varies along the reaction curve $\Im_{if}$, plays a role much as usually time does in standard quantum scattering theory. The reaction coordinate u could thus be viewed as an *intrinsic time* of the scattering.

C. Coupled-channel expression for full wavefunction and S-matrix elements

Remembering that along u the system is in translational motion, while along v and θ the motion is localized we employ the time-independent coupled-channel (CC) approach.

It is convenient to write down the intrinsic full wavefunction in the following form (see for example [37]):

$$\Phi_{K'[\varrho]}^{(+)J}(u,v,\theta) = \sum_{\bar{n}\bar{j}} G_{\bar{n}\bar{j}K'[\varrho]}^{(+)J}(u)\Xi_{\bar{n}(\bar{j})}(v;u)\Theta_{\bar{j}K'}(\theta), \quad \varrho = (njK), \tag{33}$$

and necessitate the wavefunction (33) to satisfy to initial conditions (20), the symbol $[\varrho]$ describes a set of initial quantum numbers. Note that it is standard way to obtain the close system of coupled equations for scattering (or translational) functions $G_{\varrho'[\varrho]}^{(+)J}(u)$.

The vibrational part of the wavefunction $\Xi_{n(j)}(u,v)$ forms an orthonormal basis in the variable v for each fixed value of u and satisfies the equation:

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dv^2} + \overline{U}(u,v) + \frac{\hbar^2 j(j+1)}{2\mu v^2}\right]\Xi_{n(j)}(v;u) = \epsilon_{n(j)}(u)\,\Xi_{n(j)}(v;u), \tag{34}$$

where

$$\overline{U}(u,v) = U(u,v,\theta)\big|_{\theta=0} - U_{eff}(u,v). \tag{35}$$

Recall, that $U(u,v,\theta)\big|_{\theta=0}$ corresponds to the potential energy of collinear collision.

In some situations it is useful to approximate $\overline{U}(u,v)$ such that Eq. (34) can be analytically solved (see section E). Note that the (34) in the limit $u \to -\infty$ transforms exactly into the asymptotic equation (23). Correspondingly in the limit of $u \to +\infty$ Eq. (34) describing bound state of the (out) asymptotic channel. Note that for both cases $u \to \mp\infty$ the effective potential energy $U_{eff}(u,v)$ limits to zero.

For subsequent analytical manipulations we give two important expressions for Legendre polynomials [33, 34]:

$$\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} - \frac{K^2}{\sin^2\theta}\right]\Theta_{jK}(\theta) = -j(j+1)\Theta_{jK}(\theta), \tag{36}$$

and

$$\left[\mp\frac{\partial}{\partial\theta} + (K\pm1)\cot\theta\right]\Theta_{j(K\pm1)}(\theta) = c_{jK}^{\pm}\Theta_{jK}(\theta), \quad c_{jK}^{\pm} = \left[j(j+1) - K(K\pm1)\right]^{1/2}. \tag{37}$$

Next substitute the wavefunction expression (33) into Eq. (17) taking into account (34)-(37) and multiply by $\Xi_{n'(j')}(v;u)$ and $\Theta_{j'K'}(\theta)$. Thereafter integrate over the angle θ and

coordinate v to find the following equation:

$$\left\{\left[\delta_{n'\bar{n}}\frac{d^2}{du^2}+2\left\langle\frac{\partial}{\partial u}-\frac{1}{\eta}\frac{\partial\eta}{\partial u}\right\rangle_{n'\bar{n}}\frac{d}{du}+\left\langle\frac{\partial^2}{\partial u^2}-\frac{2}{\eta}\frac{\partial\eta}{\partial u}\frac{\partial}{\partial u}\right\rangle_{n'\bar{n}}+\frac{2\mu}{\hbar^2}\left\langle\eta^2\left[E-E_{JK'}(u,v)\right]\right.\right.\right.$$

$$\left.\left.-\epsilon_{\bar{n}(\bar{j})}(u)+U(u,v)+\frac{\hbar^2\bar{j}\left(\bar{j}+1\right)}{2\mu v^2}\right]\right\rangle_{n'\bar{n}}\Bigg]\delta_{j'\bar{j}}-\frac{2\mu}{\hbar^2}\left\langle\eta^2U_{j'\bar{j}}^{K'}(u,v)\right\rangle_{n'\bar{n}}\Bigg\}G_{\bar{n}\bar{j}\,K'\,[\varrho]}^{(+)J}(u)$$

$$+\left\langle\frac{\eta^2}{q_0^2}\right\rangle_{n'\bar{n}}\delta_{j'\bar{j}}\left[C_{J\bar{j}\,K'}^{+}G_{\bar{n}\bar{j}\,(K'+1)\,[\varrho]}^{(+)J}(u)+C_{J\bar{j}\,K'}^{-}G_{\bar{n}\bar{j}\,(K'-1)\,[\varrho]}^{(+)J}(u)\right]=0, \qquad (38)$$

where $C_{JjK}^{\pm}=c_{JK}^{\pm}c_{jK}^{\pm}$ (see expressions (11) and (37)).

The equation (38) may be presented in another form:

$$\left\{\left[\delta_{n'\bar{n}}\frac{d^2}{du^2}+2\left\langle\frac{\partial}{\partial u}-\frac{1}{\eta}\frac{\partial\eta}{\partial u}\right\rangle_{n'\bar{n}}\frac{d}{du}+\left\langle\frac{\partial^2}{\partial u^2}-\frac{2}{\eta}\frac{\partial\eta}{\partial u}\frac{\partial}{\partial u}\right\rangle_{n'\bar{n}}+\frac{2\mu}{\hbar^2}\left\langle\eta^2\left[E-E_{J\bar{K}}(u,v)\right]\right.\right.\right.$$

$$\left.\left.-\epsilon_{\bar{n}(\bar{j})}(u)+U(u,v)+\frac{\hbar^2\bar{j}\left(\bar{j}+1\right)}{2\mu v^2}\right]\right\rangle_{n'\bar{n}}\Bigg]\delta_{j'\bar{j}}\delta_{K'\bar{K}}-\frac{2\mu}{\hbar^2}\left\langle\eta^2\,U_{j'\bar{j}}^{\bar{K}}(u,v)\right\rangle_{n'\bar{n}}\delta_{K'\bar{K}}$$

$$+\left\langle\frac{\eta^2}{q_0^2}\right\rangle_{n'\bar{n}}\delta_{j'\bar{j}}\left[\delta_{K'+1\,\bar{K}}\,C_{J\bar{j}\,(\bar{K}-1)}^{+}+\delta_{K'-1\,\bar{K}}\,C_{J\bar{j}\,(\bar{K}+1)}^{-}\right]\Bigg\}G_{\bar{n}\bar{j}\,\bar{K}\,[\varrho]}^{(+)J}(u)=0, \qquad (39)$$

where the summation over repeating index n' and j' are implied and we use the following notation for matrix elements:

$$\left\langle f(u)\right\rangle_{nn'}=\int_{-\infty}^{+\infty}\Xi_{n(j)}(v;u)f(u,v)\Xi_{n'(j)}^{*}(v;u)dv,$$

$$U_{jj'}^{K}(u,v)=\int_{0}^{\pi}\Theta_{jK}(\theta)\,U(u,v,\theta)\,\Theta_{j'K}(\theta)\sin\theta d\theta. \qquad (40)$$

Thus we obtain a system of N coupled second-order differential equations (38) or (39), which can be rewritten in a form of $2N$ coupled first-order ordinary differential equations system:

$$\frac{d}{du}\mathbf{F}=\begin{pmatrix}0 & \mathbf{I}\\\mathbf{A} & \mathbf{B}\end{pmatrix}\mathbf{F}, \qquad (41)$$

where

$$[\mathbf{F}(u)]_{i\leq N}=G_{\bar{n}\bar{j}\,\bar{K}\,[\varrho]}^{(+)J}(u),\quad[\mathbf{F}(u)]_{i>N}=\frac{dG_{\bar{n}\bar{j}\,\bar{K}\,[\varrho]}^{(+)J}(u)}{du},\quad\mathbf{I}=\begin{pmatrix}1\ldots0\\.\,1\,.\\0\ldots1\end{pmatrix}. \qquad (42)$$

Moreover in Eq. (41) the following denotations are made:

$$A_{n'j'K'|\bar{n}\bar{j}\bar{K}}(u) = \left[\left\langle \frac{\partial^2}{\partial u^2} - \frac{2}{\eta}\frac{\partial \eta}{\partial u}\frac{\partial}{\partial u} \right\rangle_{n'\bar{n}} + \frac{2\mu}{\hbar^2}\left\langle \eta^2 \left[E - E_{J\bar{K}}(u,v) - \epsilon_{\bar{n}(\bar{j})}(u) + U(u,v) \right. \right. \right.$$
$$\left. \left. + \frac{\hbar^2 \bar{j}\,(\bar{j}+1)}{2\mu v^2} \right] \right\rangle_{n'\bar{n}} - \left\langle \eta^2\, U_{j'\bar{j}}^{\bar{K}}(u,v) \right\rangle_{n'\bar{n}} \bigg] \delta_{j'\bar{j}}\delta_{K'\bar{K}}$$
$$\left. + \left\langle \frac{\eta^2}{q_0^2} \right\rangle_{nn'} \delta_{j'\bar{j}} \left[\delta_{K'+1\,\bar{K}}\, C_{J\bar{j}\,(\bar{K}-1)}^+ + \delta_{K'-1\,\bar{K}}\, C_{J\bar{j}\,(\bar{K}+1)}^- \right] \right.,$$

$$B_{n'j'K'|\bar{n}\bar{j}\bar{K}}(u) = -2\left\langle \frac{\partial}{\partial u} - \frac{1}{\eta}\frac{\partial \eta}{\partial u} \right\rangle_{n'\bar{n}} \delta_{j'\bar{j}}\,\delta_{K'\bar{K}}, \tag{43}$$

Now we turn to the derivation of $\boldsymbol{S}$-matrix elements using the representation for the full wavefunction (33).

As it is known the full wavefunction of three-body system is determined by the set of three quantum numbers (n, j, K). If we want to describe the full wavefunction of body system with the help of representation (33) it is necessary to demand the asymptotic condition:

$$\lim_{u\to-\infty}\sum_{n'j'} G_{n'j'K'\,[\varrho]}^{(+)J}(u) = \frac{1}{\sqrt{2\pi}}\exp\left(-ip_{nj}^-\,u\right)\delta_{nn'}\delta_{jj'}\delta_{KK'}, \tag{44}$$

to be fulfilled. It means that in the limit $u \to -\infty$, the wavefunction (33) transforms to the asymptotic wavefunction $\Phi_{njK}^{(in)J}(u,v,\theta)$ (see formula (20)).

The $\boldsymbol{S}$-matrix elements are obtained after substituting (33) into the expression (30):

$$S_{n'j'K'\leftarrow njK}(E) = \sqrt{\frac{p_{n'j'}^+}{p_{nj}^-}}\,\lim_{u\to+\infty}\sum_{\bar{n}\bar{j}} G_{\bar{n}\bar{j}K'\,[\varrho]}^{(+)J}(u)\,W_{\bar{n}n'}(u)\Lambda_{\bar{j}K'\leftarrow jK'}, \tag{45}$$

where

$$W_{n'\bar{n}}(u) = \left\langle \Xi_{\bar{n}(\bar{j})}(v;u)\Pi_{n'(j')}^{(out)}(v) \right\rangle_v, \qquad \Lambda_{\bar{j}K'\leftarrow jK'} = \left\langle \Theta_{\bar{j}K'}(\theta)\Theta_{jK'}(\theta) \right\rangle_\theta = \delta_{\bar{j}j}. \tag{46}$$

The expression for $\boldsymbol{S}$-matrix elements (45) can be simplified, if we take as basis the functions $\Xi_{n(j)}(v;u)$, which in the limit $u \to +\infty$ coincide with the orthonormal basic wavefunctions $\Pi_{\bar{n}(j)}^{(out)}(v)$. In this case we get the simplification $\lim_{u\to+\infty} W_{n'\bar{n}}(u) = \delta_{n'\bar{n}}$ and the following expression holds for $\boldsymbol{S}$-matrix elements:

$$S_{n'j'K'\leftarrow njK}(E) = \sqrt{\frac{p_{n'j'}^+}{p_{nj}^-}}\,G_{\varrho'\,[\varrho]}^{(+)J}(E;+\infty), \qquad \varrho = (njK). \tag{47}$$

So, we have now shown that the initial quantum scattering problem can be exactly reduced to the standard set of N coupled second order differential equations (38)-(39) in

a single variable u (where N is the number of channels or coupled equations). For the solution of this system of equation it is useful to represent it to the form (41). The matrix equation (41) has $2N$ linearly independent solutions. There are several standard ways in which this set of equations may be solved [3, 43, 45, 46]. The $2N$ independent solutions are then combined to give N solutions which obey the asymptotic conditions as set out in Eqs. (44). The process of combining the independent solutions to satisfy the boundary conditions automatically yields the $\textbf{\textit{S}}$-matrix elements.

D. Etalon equation method, full wavefunction and $\textbf{\textit{S}}$-matrix elements

During the development of the algorithm for numerical simulation based on aforementioned theoretical approach it is necessary to recover the scattering matrix equation (41)-(43) on the grid. The grid is formed along the reaction coordinate curve, which connects (in) and (out) scattering channels. The problem is that at each point of the grid one has to solve $M_i = n_i \times j_i$ number of one-dimensional quantum problem and by further numerical integration to find the form of the matrix equation (41) on the grid. This procedure requires huge amount of computer resource and undergoes the accumulation of computation errors. Besides matrix equation (41) in this case will be given as a numerical array, which is extremely inconvenient for numerical simulation with changing integration scale. In order to overcome this difficulty one can use the exactly solvable model for vibration states in the total wavefunction coupled-channel expression. This allows getting analytical form for one-dimensional matrix equation of reactive scattering.

So, for full wavefunction can be written another coupled-channel representation:

$$\Phi_{K'[\varrho]}^{(+)J}(u,v,\theta) = \sum_{\bar{\nu}\,\bar{j}} G_{\bar{\nu}\,\bar{j}\,K'\,[\varrho]}^{(so)J}(u)\widetilde{\Xi}_{\bar{\nu}(\bar{j})}^{(so)}(u,v)\Theta_{\bar{j}\,K'}(\theta), \qquad 0 \le \bar{\nu} < \infty, \tag{48}$$

where $\widetilde{\Xi}_{\nu(j)}^{(so)}(u,v)$ is the wavefunction of singular nonstationary (on reaction coordinate u, or later *intrinsic time* τ) quantum oscillator and satisfying the following equation [47] (later will be named the etalon equation):

$$i\hbar\frac{\partial\Xi^{(so)}}{\partial\tau} = \left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dv^2} + \left(\frac{\mu\,\omega^2(\tau)}{2}v^2 + \frac{g}{v^2}\right)\right]\Xi^{(so)}, \qquad \Xi^{(so)}(\tau;v) \equiv \widetilde{\Xi}^{(so)}(u,v),$$

$$\tau = u/v_0, \qquad g = \frac{\hbar^2}{2\mu}j(j+1), \qquad 0 < v < \infty, \qquad -\infty < u,\tau < +\infty. \tag{49}$$

Note that $v_0 = a_0 \omega_i$ (where a_0 is a Bhor radius, for explanation ω_i see (53)) give the characteristic speed by coordinate of localized motion v.

The Eq. (49) can be solved exactly [48] for values $v \geq 0$:

$$\Xi_{\nu(j)}^{(so)}(\tau; v) = \left[2\left(\frac{\mu}{\hbar \sigma^2}\right)^{a+1} \frac{\Gamma(n+1)}{\Gamma(n+a+1)}\right]^{1/2} v^{a+1/2} \exp\left(-2i\nu\gamma + i\frac{\mu}{2\hbar}\frac{\dot\sigma}{\sigma}v^2\right) L_\nu^a\left(\frac{\mu\dot\gamma}{\hbar}v^2\right),$$

$$\dot\sigma = \frac{d\sigma}{d\tau}, \qquad \dot\gamma = \frac{d\gamma}{d\tau}, \qquad a = \frac{1}{2}\left(1 + \frac{8\mu g}{\hbar^2}\right)^{1/2}. \tag{50}$$

It is significant that the solution (50) may be analytically continued to the infinite numerical axis $-\infty < v < +\infty$ (see particularly ([47])). In (50) the function $\gamma(\tau) = \int^u |\sigma(\tau)|^{-2} d\tau$ is the argument of complex function σ which is a solution of classical oscillator problem:

$$\ddot\sigma + \omega^2(\tau)\sigma = 0. \tag{51}$$

For further investigations it is useful to have an analytically solvable model for function $\sigma(\tau)$. In particularly the Eq. (51) may be integrated exactly if the frequency is described by following model form (see Appendix E) [49]:

$$\omega^2(\tau) = A_0 + A_1 \tanh(\lambda\tau), \tag{52}$$

where A_0, A_1 and λ are some adjusting constants, which can be chosen to be most suitable for numerical simulations. As it is evident from formula (52), $\lim_{u,\tau\to\mp\infty} \omega^2(\tau) = \omega_{i,f}^2$ and corresponding asymptotic solutions of Eq. (51) are:

$$\sigma(\tau) \underset{\tau\to-\infty}{\sim} \omega_i^{-1/2} e^{i\omega_i\tau},$$

$$\sigma(\tau) \underset{\tau\to+\infty}{\sim} \omega_f^{-1/2}\left(C_1 e^{i\omega_f\tau} - C_2 e^{-i\omega_f\tau}\right), \qquad \omega_{i,f}^2 = A_0 \mp A_1, \tag{53}$$

where $\omega_{i,f}$ are coefficients at second terms of expansion series in corresponding asymptotic bound states potential energies (see Eq. (23)). The coefficients $C_{1(2)}$ are some complex numbers which are found by the solution of Eq. (51) in the limit $\tau \to +\infty$. The constraint $|C_1|^2 - |C_2|^2 = 1$ is hashed at the numbers C_1 and C_2, which is followed by commutation correspondence.

Using this fact it is easy to calculate bound-state energy in asymptotic channels $\epsilon_{\nu(j)} = \hbar\omega_{i,f}(2\nu + a + 1)$ and the asymptotic form of the etalon wavefunction (50). In particular, in the (in) asymptotic channel:

$$\Xi_{\nu(j)}^{(so)}(\tau; v) \underset{\tau\to-\infty}{\sim} \Xi_{\nu(j)}^{(-)}(\tau; v) =$$

$$\left[2\left(\frac{\mu\omega_i}{\hbar}\right)^{a+1} \frac{\Gamma(n+1)}{\Gamma(n+a+1)}\right]^{1/2} v^{a+1/2} \exp\left(-2i\nu\omega_i\tau - \frac{\mu\omega_i}{2\hbar}v^2\right) L_\nu^a\left(\frac{\mu\omega_i}{\hbar}v^2\right). \tag{54}$$

In the Eq. (54) $L_\nu^a(\hbar^{-1}\mu\dot\gamma v^2)$ is Lager polynomial and the wavefunctions $\Xi_{\nu(j)}^{(so)}(\tau;v)$ form an orthonormal basis: $\int_0^\infty \Xi_{\nu(j)}^{(so)}(\tau;v)\Xi_{\lambda(j)}^{(so)*}(\tau;v)dv = \delta_{\nu\lambda}$.

When $g = 0$ ($a = 1/2$) the wavefunctions (54) describe the nonstationary oscillator with wall at the beginning of coordinate [50]. It is well know that the wavefunction of this system coincides with odd functions of harmonic oscillator in view of identity $H_{2\nu+1}(x) = (-1)^\nu 2^{2\nu+1}\nu! x L_\nu^{1/2}(x^2)$ (see for example [51]). Nevertheless the Eq. (49) have another type solution too, which coincides with even wavefunctions of harmonic oscillator [52].

So, in case of $g = 0$ the solution of etalon equation (49) is wavefunction of quantum harmonic oscillator depending on time (in this case *intrinsic time* τ) frequency [47, 53]:

$$\Xi_\nu^{(so)}(\tau;v) = \left(\frac{\dot\sigma^*}{2\sigma}\right)^{\nu/2}(\nu!\sigma\sqrt\pi)^{-1/2}\exp\left(i\frac{\dot\sigma}{2\sigma}v^2\right)H_\nu\left(\frac{v}{|\sigma|}\right). \tag{55}$$

Now comparing representations (34) and (48) is easy to find the following relation between reactive scattering functions $G_{\tilde n \tilde j\, K'\,[\varrho]}^{(+)J}(u)$ and $G_{\tilde n \tilde j K'\,[\varrho]}^{(so)J}(u)$:

$$G_{\tilde n \tilde j\, K'\,[\varrho]}^{(+)J}(u) = \sum_{\bar\nu} C_{\bar\nu \bar n(\bar j)}(u)G_{\bar\nu \tilde j\, K'\,[\varrho]}^{(so)J}(u), \tag{56}$$

where matching coefficients $C_{\bar\nu\bar n(\bar j)}(u)$ is defined by formula:

$$C_{\bar\nu\bar n(\bar j)}(u) = \int_{-\infty}^{+\infty}\Xi_{\bar\nu(\bar j)}^{(so)}(uv_0^{-1};v)\Xi_{\bar n(\bar j)}^*(u,v)dv. \tag{57}$$

Using (57) in the limit $u \to -\infty$ for definition of asymptotic conditions for the function $G_{\bar\nu \tilde j\, K'\,[\varrho]}^{(so)J}(u)$ the system of linear equations can be obtained:

$$\begin{cases} \sum_{\bar\nu} C_{\bar\nu 0(\bar j)}^-(u)\, G_{\bar\nu \tilde j\, K'\,[\varrho]}^{(so)J}(u) = 0, \\ \qquad \cdots \qquad\qquad , \\ \sum_{\bar\nu} C_{\bar\nu \bar n(\bar j)}^-(u)\, G_{\bar\nu \tilde j\, K'\,[\varrho]}^{(so)J}(u) = o(u), \\ \qquad \cdots \qquad\qquad , \\ \sum_{\bar\nu} C_{\bar\nu \bar m(\bar j)}^-(u)\, G_{\bar\nu \tilde j\, K'\,[\varrho]}^{(so)J}(u) = 0, \end{cases} \tag{58}$$

where m defines the number of vibrational states in the (in) channel in the same way as $o(u) = \left(2\pi\right)^{-1/2}\exp\left(-ip_{nj}^- u\right)$ and $C_{\bar\nu\bar n(\bar j)}^-(u) = \int_{-\infty}^{+\infty}\Xi_{\bar\nu(\bar j)}^{(-)}(uv_0^{-1};v)\widetilde\Xi_{\bar n(\bar j)}^*(u,v)dv$.

In the system (58) the number of equations is finite while the number of unknown quantities is infinite. For exact definition of problem (58) we have to demand following conditions:

$$G_{\bar\nu \tilde j\, K'\,[\varrho]}^{(so)J}(u) \equiv 0, \quad \nu > m. \tag{59}$$

Now substituting (48) into (17) and after simple analytical calculation we can get a new equation for reactive scattering:

$$
\begin{aligned}
\Bigg\{ & \delta_{j'\bar{j}}\,\delta_{K'\bar{K}}\Bigg[\delta_{\nu'\bar{\nu}}\frac{d^2}{du^2} + 2\left\langle\frac{\partial}{\partial u} - \frac{1}{\eta}\frac{\partial\eta}{\partial u}\right\rangle_{\nu'\bar{\nu}}\frac{d}{du} + \left\langle\frac{\partial^2}{\partial u^2} - 2\left(\frac{1}{\eta}\frac{\partial\eta}{\partial u} + i\frac{\mu}{\hbar}v_0\right)\frac{\partial}{\partial u}\right\rangle_{\nu'\bar{\nu}} \\
& + \frac{2\mu}{\hbar^2}\left\langle\eta^2\Big[E - E_{J\bar{K}}(u,v) - U_{eff}(u,v) + \frac{1}{2}\mu\omega^2 v^2 + \frac{\hbar^2\bar{j}(\bar{j}+1)}{2\mu v^2}\Big]\right\rangle_{\nu'\bar{\nu}}\Bigg] \\
& + \delta_{\bar{j}j'}\left\langle\frac{\eta^2}{q_0^2}\right\rangle_{\nu'\bar{\nu}}\Big[\delta_{K'+1\,\bar{K}}\,C^{+}_{J\bar{j}\,\bar{K}-1} + \delta_{K'-1\,\bar{K}}\,C^{-}_{J\bar{j}\,\bar{K}+1}\Big] \\
& - \frac{2\mu}{\hbar^2}\left\langle\eta^2 U^{\bar{K}}_{j'\bar{j}}(u,v)\right\rangle_{\nu'\bar{\nu}}\delta_{K'\bar{K}}\Bigg\}G^{(so)J}_{\bar{\nu}\bar{j}\,\bar{K}\,[\varrho]}(u) = 0.
\end{aligned}
\tag{60}
$$

In this case the summation over repeating index $\bar{\nu}$ is implied and we use the following notation for matrix elements:

$$
\left\langle f(u)\right\rangle_{\nu\nu'} = \int_{-\infty}^{+\infty}\Xi^{so}_{\nu(j)}(uv_0^{-1};v)f(u,v)\Xi^{so*}_{\nu'(j)}(uv_0^{-1};v)\,dv.
\tag{61}
$$

Remind that the system of second order differential Eq. (60) may be written in the first order form of type (41)-(43).

Finally, taking into account (44)-(46) (48) and (57) one can find the new expression for $\boldsymbol{S}$-matrix elements:

$$
\begin{aligned}
S_{n'j'K'\leftarrow njK}(E) &= \sqrt{\frac{p^{+}_{n'j'}}{p^{-}_{nj}}}\,\lim_{u\to+\infty}\sum_{\bar{\nu}\,\bar{n}\,\bar{j}}G^{(so)}_{\bar{\nu}\bar{j}\,K'\,[\varrho]}(u)C_{\bar{\nu}\bar{n}(\bar{j})}(u)W_{\bar{n}n'}(u)\Lambda_{j'K'\to\bar{j}\,K'} \\
&= \sqrt{\frac{p^{+}_{n'j'}}{p^{-}_{nj}}}\sum_{\bar{\nu}}G^{(so)}_{\bar{\nu}j'K'\,[\varrho]}(E;+\infty)C_{\bar{\nu}n'(j')}(+\infty).
\end{aligned}
\tag{62}
$$

So, we found a new analytical expression for the $\boldsymbol{S}$-matrix elements of reactive scattering (62) with the help of exactly solvable etalon equation (49) and we will call it *etalon equation method*. Obviously this method is favorable for numerical simulation. Particularly computation of $\boldsymbol{S}$-matrix elements (62) in this case is relatively simple too.

IV. CONCLUSION

The introduction of *natural collision coordinates* by Marcus [18] was intended to simplify quantum reactive scattering calculations. In spite of significant efforts [19, 20, 21] the application of this method to $3D$ reactive scattering has encountered considerable difficulties,

and as a consequence the investigations in this direction ceased in 1988 (see for example report [3]). In particular, the following two problems can be indicated:

1. For an atom-diatom arrangement reaction $A + BC$ in $3D$, at every conserved total angular momentum J, the vibrational coordinate v (see FIG. 3) becomes a $2D$ (ro-vibrational) surface in the $3D$ intrinsic space which specifies the size and the shape of three-atom triangle. It is significant that this surface has extremely complicated the metric properties and can be investigated with the help of difficult numerical calculations [22].

2. The third arrangement reaction $AC+B$ (see schema 1) must also be included in the $3D$ computation schema. However, this leads to problems in the understanding of trans-lational *reaction coordinate* idea. Moreover, technical difficulties arise by *matching surfaces* between the three arrangement channels.

Nevertheless the mentioned difficulties either can be overcame in the intrinsic $3D$ space or they do not play an essential role in the framework of this consideration.

Hence, if we define three different curves of the *reaction coordinate* $\Im_{if}$ analogously to (5) by the way they connect different asymptotic subspaces (different reactant and product channels) one can describe all the scattering channels (see schema 1). From the other side, by defining this curve and correspondingly NCC system carefully on the case of collinear collision all possible configuration of reactive scattering may be described.

In recent articles [29, 30, 31], one of the authors together with colleagues have analyzed in detail the difficulties arising in the formulation of quantum scattering theory in NCC system.

In particular, it was shown for the case of a collinear scattering process in NCC system that a procedure similar to that described above for the $3D$ case could effectively yield the exact $\boldsymbol{S}$-matrix.

In this article the quantum reactive scattering theory in curvilinear reaction coordinates has been generalized to the $3D$ case.

We have started with Schrödinger equation of thee-body system in Jacobi coordinates (10). Using the coordinate transformation given in Eqs. (5)-(8) this equation has been transformed into the NCC system. The reaction coordinate u (or τ) may be considered as a chronological parameter in the theory (i.e. *intrinsic time*), and plays a role analogous to that

of time in standard time-dependent scattering theory. Representing the full wavefunction of three-body system by standard coupled-channel form (33) the initial $3D$ multi-channel quantum scattering problem (17) with correspondingly initial and border conditions (20) may be reduced to an inelastic single-arrangement problem Eq. (38)-(39) or (41)-(43). As a result of this reducing after the solution of system of Eq. (41)-(43) on a set of points u of curve of reaction coordinate $\Im_{if}$ (grid) the full wavefunction and all transition $\boldsymbol{S}$-matrix elements are found simultaneously (see expression for $\boldsymbol{S}$-matrix elements (47)).

Another direction of investigation of Schrödinger Eq. (17) is the representation of solution for full wavefunction of three-body system in the coupled-channel form (48) combined with the exact solvable *etalon equation method* (see Eqs. (49)-(50)). Recall that etalon equation describes the localization properties of full wavefunction along the curve of reaction coordinate $\Im_{if}$. This method reduces the $3D$ quantum multichannel scattering problem to inelastic single-arrangement problem too. Still, the initial conditions for the system of differential equations (60) in this case are a little bit complicated and can be found by the solution of linear algebraic equations system (58)-(59).

Note that this is an important theoretical result, which seems to very useful for numerical calculations. Remind that in traditional approached the $1D$ scattering problem Eq. (34)-(35) is constructed after very grate volume of grid computations of $1D$ Schrödinger problem along the reaction coordinate.

The main theoretical advantage is that the wavefunction and all the body-fixed $\boldsymbol{S}$-matrix elements are determined from the solution of standard coupled differential equations in only one variable u (the scattering coordinate) simultaneously. The body-fixed $\boldsymbol{S}$-matrix is used to determine all the differential and integral state-to-state reactive scattering cross sections of the system (see formulas (30) and (31)).

It is obvious that on the basis of developed $\boldsymbol{S}$-matrix representations the maximally-possible effective parallel algorithms for direct numerical simulation of $3D$ reactive quantum scattering problem may be elaborated. Particularly numerical solution of both systems of inelastic scattering equations (39) or (41)-(43) and (60) can be realized with the help of the $\boldsymbol{R}$-matrix propagation method simultaneously yields the full wavefunction and all $\boldsymbol{S}$-matrix elements without further calculations.

Finally, we would like to note that the usage of NCC system in quantum multichannel scattering theory will permit to carry out similar type reduction for any amount of atoms.
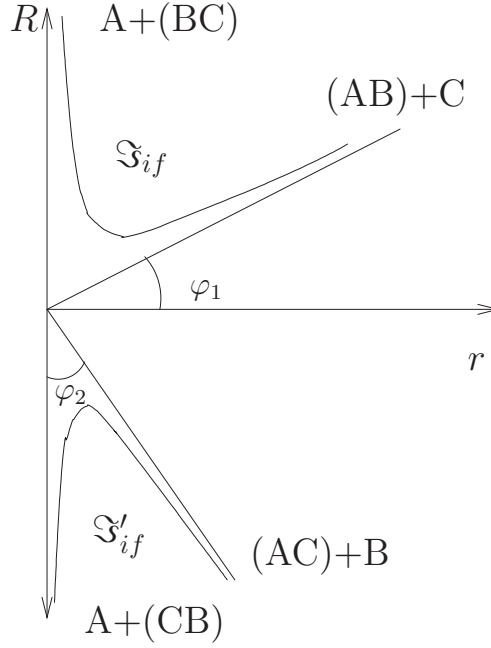
FIG. 4: *The curve of reaction coordinates for two different exchange reactions on a collinear colli-sions plane (R, r). It is obvious that in this plane there are not interferences between two exchange reaction channels. Recall that angles φ_1 and φ_2 are given by formulas $cot\varphi_1 = \left[m_A m_C / m_B M \right]^{1/2}$ and $cot\varphi_2 = \left[m_A m_B / m_C M \right]^{1/2}$.*

This will essentially simplify the calculation.

V.   ACKNOWLEDGMENTS

APPENDIX A: CHOICE OF 3D NCC SYSTEM

Two collinear collision configurations between free particle A and bound pair (BC) schematically may be represented on the plane of Jacobi coordinates (R, r) in the following case (see FIG. 4):   The smooth curves (coordinate reactions) $\Im_{if}$ and $\Im'_{if}$ in figure con-nect correspondingly reagent and product asymptotic subspaces in the collinear collisions
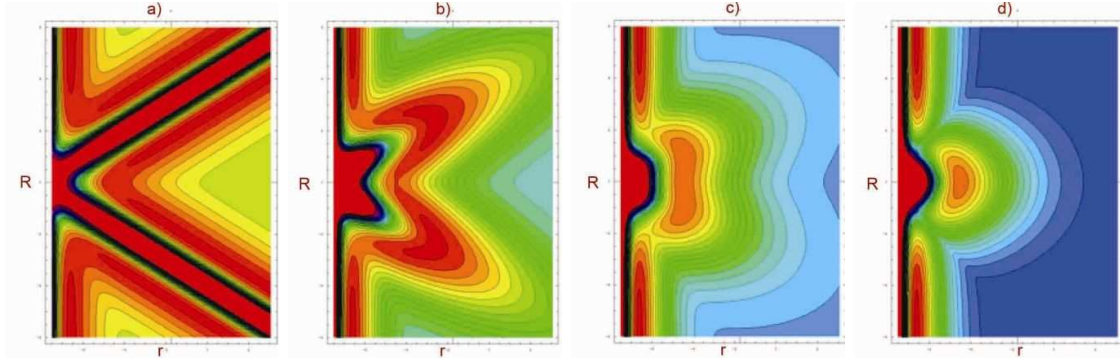
FIG. 5: *Energy surfaces of reactive system $H + H_2$ in the plane of Jacobi coordinates (R, r) for different angles $\theta = 0^0, 30^0, 60^0, 90^0$. As it is evidently in the plane a) two reaction channels are opened while on the planes b), c), d) only excitation channels are opened. Note that it is a universal property which follows from kinematic geometry of scattering and doesn't depend on what A, B and C particles are interacted.*

$A + (BC)$ and $A + (CB)$. It is obvious that in this case the different reaction channels are isolated and there is no interference between them. The illustration of this fact is shown on the example of *ab initio* PES, termed LSTH, type potential energy surface for reactive system $H + H_2$ (see FIG. 5a) [56, 57]. When the Jacobi angle is fixed $\theta \in (0, \pi)$, going along the curve $\Im_{if}$ or $\Im'_{if}$ we can't come to mentioned products subspaces. In other words the exchange reaction channels on the plane (R, r) in this case are closed and this is an universal kinematic property of scattering and doesn't depend from particles sort (see FIG. 5b-5d).

However, in this case the reaction goes out of mentioned plane in $3D$ space (see FIG. 6a-6d and FIG. 7a-7d). As kinematic analysis shows, the $3D$ region, where the probability of reactive scattering processes is concentrated, is essential around the collinear collision plane (R, r). Moreover, this region is compressed to the plan (R, r) as system is evolving along coordinate reaction curve $\Im_{if}$ (or $\Im'_{if}$) to the asymptotic subspace of products. Recall that all topological properties of reaction surface, which are in Jacobi coordinates system, are conserved in $3D$ NCC system too.

So, the $3D$ NCC system, which is connected with the reaction coordinate curves $\Im_{if}$ or $\Im'_{if}$, describes uniquely $3D$ part of configuration space, where multichannel scattering process is concentrated.
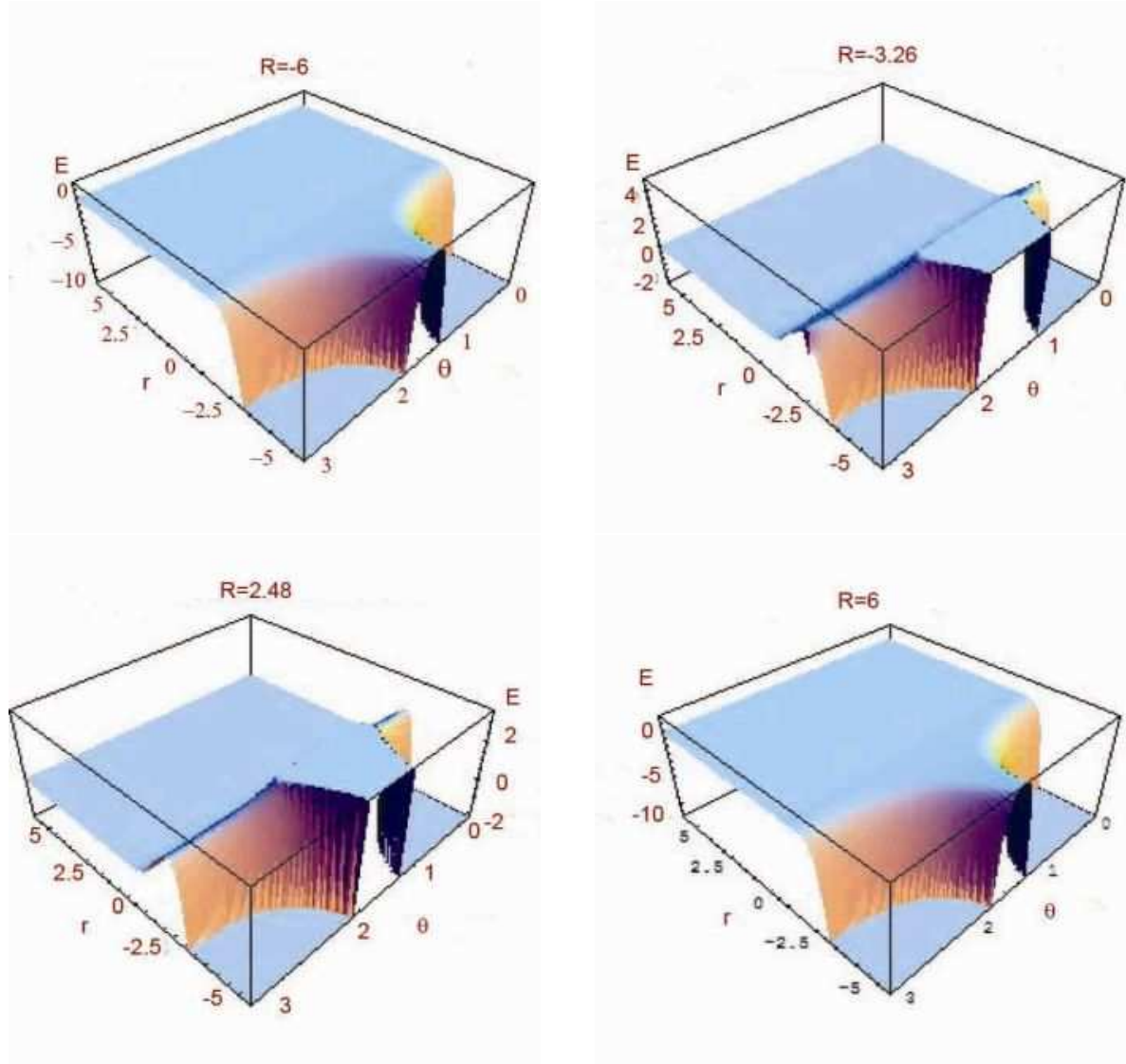
FIG. 6: *Energetic surfaces of reactive system $H + H_2$ in the coordinates plane (r, θ) for different fixing coordinates R. It is evident from pictures in the strong interaction region (the region where interactions between all particles are essentially) that there are two potential holes one around the angle $\theta = 0$ (or collinear configuration $A + (BC)$) and the second around the angle $\theta = \pi$ (or collinear configuration $A + (CB)$). It is obviously that during the evolution the three body system with big probabilities can fall within first or second hole.*
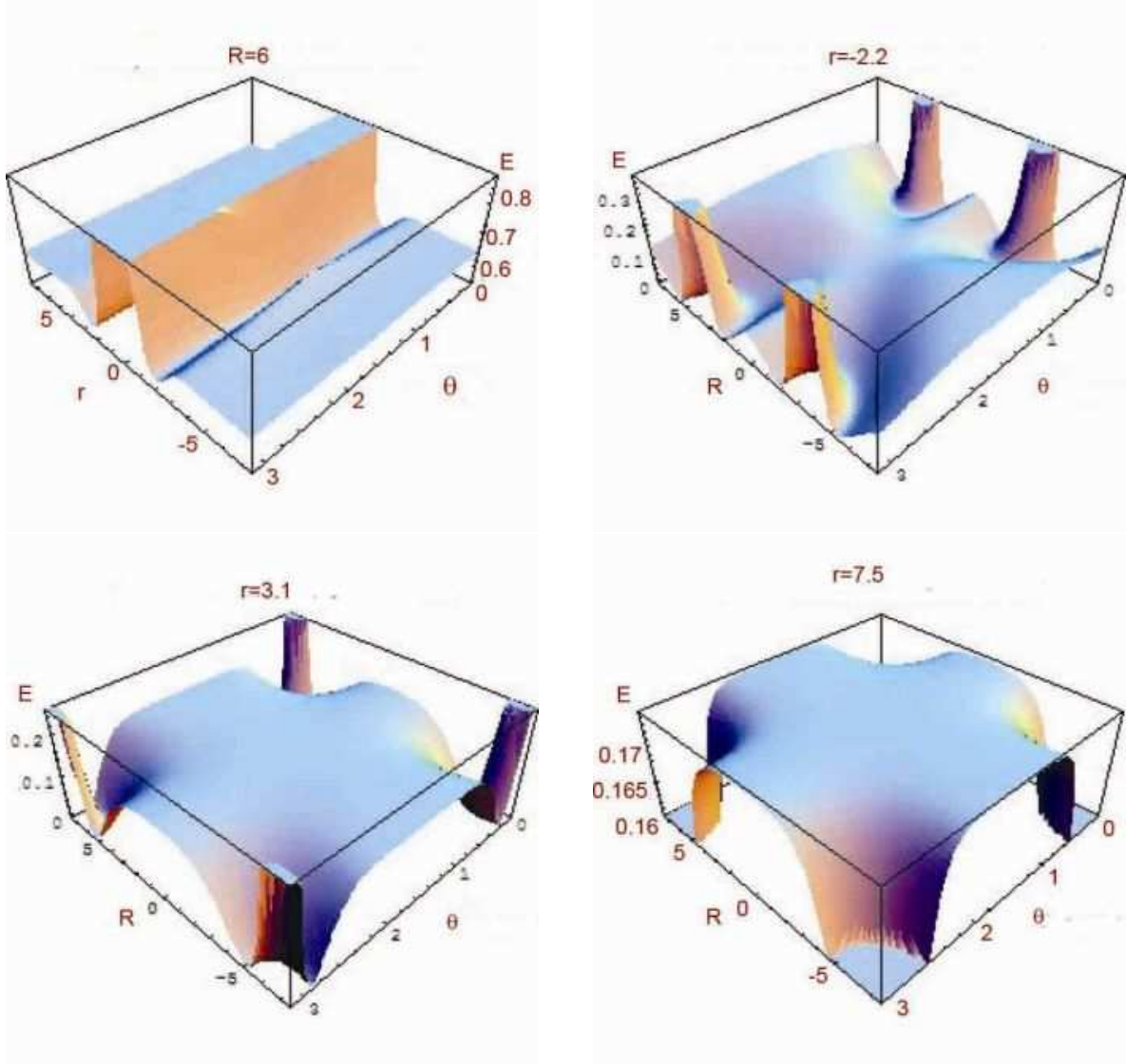
FIG. 7: Energetic surfaces of reactive system $H + H_2$ in the coordinates plane (R, θ) for different fixing coordinates r. On these energetic surfaces are generated gradients which push on the three body system to collinear configurations.

APPENDIX B: MASS-SCALED DISTANCES BETWEEN THREE-BODY

For right introducing of NCC system it is necessary to connect the curve of reaction coordinate $\Im_{if}$ in the plan of (q_0, q_1) with two equilibrium distances of diatoms of (in) and (out) asymptotic channels. Let us consider the distant between A and B particles in the

(*in*) Jacobi coordinates (see FIG. 1):

$$R_{AB} = \sqrt{R_\alpha^2 - 2\rho R_\alpha r_\alpha \cos\theta_\alpha + (\rho r_\alpha)^2}, \quad \rho = \frac{m_C}{m_b + m_C}, \tag{B1}$$

where indexes which note channels are admitted. After simple transformations taking into account (2) and (3) from (B1) we can find:

$$R_{AB} = \sqrt{\lambda^{-2} q_0^2 - 2\rho q_0 q_1 \cos\theta + \lambda^2 (\rho q_1)^2} = \lambda^{-1} \sqrt{q_0^2 - 2 b q_0 q_1 \cos\theta + (b q_1)^2} = \lambda^{-1} q_2, \tag{B2}$$

where $b = \rho \lambda^2 = \cot\varphi$, and q_2 is mass-scaled distance between A and B particles. Now we can investigate the asymptotic behavior of mass-scaled distance q_2. From Eq. (B2) with taking into account (5) in the (*in*) channel (in the limit of $q_1^c \to q_{eq}^-$) may be find:

$$q_2\big|_{\Im_{if}} - q_0^c = \left(q_2^c - q_0^c\right)\big|_{q_1^c \to q_{eq}^-} = -b q_{eq}^- \cos\theta. \tag{B3}$$

From which is following that curve $\Im_{if}$ in the reactant (*in*) channel comes to equilibrium diatom (BC) distance q_{eq}^-.

Because Jacobi scattering angle which is defined in (*in*) channel in the (*out*) channel is limited to zero ($\theta \to 0$) from (B2) and (5) can be find:

$$q_2^c\big|_{q_1^c \to \infty} = q_0^c - b q_1^c = q_{eq}^+, \tag{B4}$$

which is mean that in product (*out*) channel curve $\Im_{if}$ coming to equilibrium distance q_{eq}^+ of (AB) diatom.

So, the definition of curve of *reaction coordinate* $\Im_{if}$ which is defined by formulas (5) and (6) satisfies the aforementioned asymptotic conditions.

Completely note that definition of curve of reaction coordinate $\Im'_{if}$ for exchange reaction $A + (CB) \to (AC) + B$ we can find from (5) putting instead of constants b and q_{eq}^+ constants $(1 - b)$ and $\widetilde{q}_{eq}^+$ correspondingly, where $\widetilde{q}_{eq}^+$ is an equilibrium distance between pair (AC) in the asymptotic channel $(q_1^c \to +\infty)$.

As for the dissociation reaction $A + (BC) \to A + B + C$ it can be described by term of both NCC systems. Only in this case we must remember that Jacobi angle does not limit to zero and can have any value.

APPENDIX C: CALCULATION OF METRIC TENSOR IN CURVILINEAR RE-ACTION COORDINATES

Let us calculate the transformation between Jacobi scaled and NCC coordinates systems in the plan (q_0, q_1). As well known covariant metric tensor defined by:

$$\gamma_{ij} = \sum_{k=0}^{1} \frac{\partial q_k}{\partial x^i} \frac{\partial q_k}{\partial x^j}, \qquad \{x^j\} = (x^0, x^1) \equiv (u, v), \quad i, j, k = 0, 1. \tag{C1}$$

In order to do this, first we calculate the non-diagonal terms. Using (5) and (6), as well as the fact that x^0 and x^1 are orthogonal, one can obtain from (C1) the following expression:

$$\gamma_{01} = \gamma_{10} = -\left(\frac{dq_0^c}{du} - v \cos \phi(u) \frac{d\phi}{du} \right) \sin \phi + \left(\frac{dq_1^c}{du} - v \sin \phi(u) \frac{d\phi}{du} \right) \cos \phi$$

$$= -\frac{dq_0^c}{du} \sin \phi(u) + \frac{dq_1^c}{du} \cos \phi(u). \tag{C2}$$

Requiring orthogonality of the NCC we set $\gamma_{01} = \gamma_{10} = 0$, giving:

$$\frac{dq_0^c}{dq_1^c} = \cot \phi(u), \tag{C3}$$

on the curve $\Im_{ij}$. Note that the function $\phi(u)$ has a simple geometrical meaning: it corresponds to the angle between the tangential to the reaction coordinate and q_1. From (C3) it is easy to get:

$$\sin \phi(u) = \frac{1}{\sqrt{1 + \left(dq_0^c / dq_1^c \right)^2}}, \qquad \cos \phi(u) = \frac{dq_0^c / dq_1^c}{\sqrt{1 + \left(dq_0^c / dq_1^c \right)^2}}. \tag{C4}$$

After derivation $\sin \phi(u)$ by variable u with taking into account (C4) one can write:

$$\left(\sin \phi(u) \right)_{;u} = \cos \phi(u) \frac{d\phi}{du} = -\frac{dq_0^c / dq_1^c}{\left\{ 1 + \left(dq_0^c / dq_1^c \right)^2 \right\}^{3/2}} \frac{d}{du} \left(\frac{dq_0^c}{dq_1^c} \right). \tag{C5}$$

Using equations (5) and (6) from (C5) may be find:

$$\left(\sin \phi(u) \right)_{;u} = -\frac{2a}{\left(q_1^c - q_{eq}^- \right)^3} \frac{b - a / \left(q_1^c - q_{eq}^- \right)^2}{b + a / \left(q_1^c - q_{eq}^- \right)^2} \left\{ 1 + \left[b - a / \left(q_1^c - q_{eq}^- \right)^2 \right]^2 \right\}^{-3/2}, \tag{C6}$$

where symbol $()_{;s}$ is denoted derivation.

The expression for function $\left(\sin \phi(u) \right)_{;u}$ correspondingly have a form:

$$\left(\cos \phi(u) \right)_{;u} = -\frac{2a}{\left(q_1^c - q_{eq}^- \right)^3} \frac{1}{b + a / \left(q_1^c - q_{eq}^- \right)^2} \left\{ 1 + \left[b - a / \left(q_1^c - q_{eq}^- \right)^2 \right]^2 \right\}^{-3/2}. \tag{C7}$$

For matrix element γ_{00} from (C1) may be find expression:

$$\gamma_{00} = \left(\frac{\partial q_0}{\partial u}\right)^2 + \left(\frac{\partial q_1}{\partial u}\right)^2 = \left(\frac{dq_0^c}{du} - v\cos\phi(u)\frac{d\phi}{du}\right)^2 + \left(\frac{dq_1^c}{du} - v\sin\phi(u)\frac{d\phi}{du}\right)^2. \quad \text{(C8)}$$

Substituting the derivatives (C6) and (C7) into (C8) we obtain:

$$\gamma_{00} = \left[1 + K(u)v\right]^2 \left(\frac{ds}{du}\right)^2, \quad \text{(C9)}$$

where $K(u)$ is Gaussian curvature of reaction coordinate curve $\Im_{if}$ and s is correspondingly the length along the $\Im_{if}$:

$$K(u) = \frac{2a}{\left(q_1^c - q_{eq}^-\right)^3}\left\{1 + \left[b - a/\left(q_1^c - q_{eq}^-\right)^2\right]^2\right\}^{-3/2},$$

$$\left(\frac{ds}{du}\right)^2 = \left\{1 + \left[b - a/\left(q_1^c - q_{eq}^-\right)^2\right]^2\right\}\left\{b + a/\left(q_1^c - q_{eq}^-\right)^2\right\}^{-2}. \quad \text{(C10)}$$

Note that the Lamé coefficient is given by $\eta = \sqrt{\gamma_{00}}$.

We also note that the elements $\gamma_{02} = \gamma_{02} = \gamma_{12} = \gamma_{21}$ vanish. Remind that the second diagonal element γ_{11} may be obtained by using (5)-(6) and (C1):

$$\gamma_{11} = \left(\frac{\partial q_0}{\partial v}\right)^2 + \left(\frac{\partial q_1}{\partial v}\right)^2 = 1. \quad \text{(C11)}$$

Thus the metric tensor γ_{ij} is diagonal. Finally we note that the covariant tensor is defined as:

$$\gamma^{ij} = B_{ij}/\gamma, \quad \gamma = Det\left(\gamma_{ii}\right) = \gamma_{00}\gamma_{11} = \gamma_{00}, \quad \text{(C12)}$$

where B_{ij} is the algebraic complement to γ_{ij}.

APPENDIX D: S-MATRIX CONTRACTION BY REACTION COORDINATE (INTRINSIC TIME) FORMALISM

Between full wavefunctions in the different body-fixed systems the following transformation may be written (see (24)):

$$\sum_{\bar{K}} \rho_\alpha^{-1/2}\Phi_{nj\bar{K}}^{(\pm)J}(u_\alpha, v_\alpha, \theta_\alpha)D_{\bar{K}K}^J(\Omega_\alpha) = \sum_{\bar{K}} \rho_\beta^{-1/2}\Phi_{nj\bar{K}}^{(\pm)J}(u_\beta, v_\beta, \theta_\beta)D_{\bar{K}K}^J(\Omega_\beta). \quad \text{(D1)}$$

Next we multiply the equation (D1) by the Wigner $D_{\bar{K}K}^{J*}(\Omega)$-function and integrate, using the volume element $d\Omega = \sin\zeta_2\, d\zeta_1 d\zeta_2 d\zeta_3$. With help of formulas:

$$\int D_{M_1 M_1'}^{J_1*}(\zeta_1, \zeta_2, \zeta_3)D_{M_2 M_2'}^{J_2}(\zeta_1, \zeta_2, \zeta_3)\, d\Omega = \frac{8\pi^2}{2J_1 + 1}\delta_{J_1 J_2}\delta_{M_1 M_2}\delta_{M_1' M_2'}$$

and (25) we get:

$$\Phi_{njK}^{(\pm)J}(u_\alpha, v_\alpha, \theta_\alpha) = \left(\frac{\rho_\alpha}{\rho_\beta}\right)^{1/2} \sum_{\bar{K}} d_{\bar{K}K}^J(\vartheta)\Phi_{nj\bar{K}}^{(\pm)J}(u_\beta, v_\beta, \theta_\beta). \tag{D2}$$

Now we are multiplying the equation (19) on the (out) asymptotic state (21)-(22) and integrating it by coordinates v and θ after which in the limit $u \to +\infty$ the scattering matrix elements may be found:

$$\lim_{u \to +\infty} \left\langle \Phi_{njK}^{(+)J}(u_\alpha, v_\alpha, \theta_\alpha)\Phi_{n'j'K'}^{(out)J}(u_\beta, v_\beta, \theta_\beta) \right\rangle_{v\theta} =$$

$$\sum_{\tilde{n}\tilde{j}\tilde{K}} S_{\tilde{n}\tilde{j}\tilde{K} \leftarrow njK}^J \lim_{u \to +\infty} \left\langle \Phi_{\tilde{n}\tilde{j}\tilde{K}}^{(-)J}(u_\beta, v_\beta, \theta_\beta)\Phi_{n'j'K'}^{(out)J}(u_\beta, v_\beta, \theta_\beta) \right\rangle_{v\theta}$$

$$= \sum_{\tilde{n}\tilde{j}\tilde{K}} \delta_{n'\tilde{n}} \delta_{j'\tilde{j}} \delta_{K'\tilde{K}} S_{\tilde{n}\tilde{j}\tilde{K} \leftarrow njK}^J = S_{n'j'K' \leftarrow njK}^J. \tag{D3}$$

So we found a new expression for the scattering $\boldsymbol{S}$-matrix elements between (in) and (out) asymptotic states which are defined on different α and β surfaces:

$$S_{n'j'K' \leftarrow njK}^J = \lim_{u \to +\infty} \left\langle \Phi_{njK}^{(+)J}(u_\alpha, v_\alpha, \theta_\alpha)\Phi_{n'j'K'}^{(out)J}(u_\beta, v_\beta, \theta_\beta) \right\rangle_{v\theta}. \tag{D4}$$

Note that in this approach coordinate of translational motion u plays similar role as a usual time in the standard scattering theory and will be called *intrinsic time*.

Now it is important to find the $\boldsymbol{S}$-matrix elements form in the one coordinates system α or correspondingly β.

Putting the expression for overall wavefanction (27) in the (D4) we can find:

$$S_{n'j'K' \leftarrow njK}^J(E) = \lim_{u \to +\infty} \sqrt{\frac{p_{n'j'}^+}{p_{nj}^-}} \left\langle \sum_{\bar{K}} d_{\bar{K}K}^J(\vartheta)\Phi_{nj\bar{K}}^{(+)J}(u, v, \theta)\Phi_{n'j'K'}^{(out)J}(u, v, \theta) \right\rangle_{v_\beta\theta_\beta}. \tag{D5}$$

Since the angle ϑ between vectors $\mathbf{q}_{0\alpha}$ and $\mathbf{q}_{0\beta}$ in the (out) channel (when $u \to +\infty$) is limited to π and taking into account that:

$$d_{(\bar{K}-K)}^J(\pi) = (-1)^{\bar{K}-K}\delta_{\bar{K}K}, \tag{D6}$$

it is easy to get the expression for $\boldsymbol{S}$-matrix elements:

$$S_{n'j'K' \leftarrow njK}^J(E) = \sqrt{\frac{p_{n'j'}^+}{p_{nj}^-}} \lim_{u \to +\infty} \left\langle \Phi_{njK}^{(+)J}(u, v, \theta)\Phi_{n'j'K'}^{(out)J}(u, v, \theta) \right\rangle_{v\theta}. \tag{D7}$$

Besides in the expression (D7) the coefficient $\sqrt{p_{\tilde{n}j}^+/p_{nj}^-}$ is described flux normalization constant:

$$\sqrt{\frac{p_{n'j'}^+}{p_{nj}^-}} = \lim_{u \to +\infty} \left(\frac{\rho_\alpha}{\rho_\beta}\right)^{1/2}. \tag{D8}$$

In another words we proved that it is possible to represent the full and asymptotic wavefunctions in term of same NCC system without matching between reactant and product channels. It is very important result of developed theory.

So, the matrix elements $S_{n'j'K' \leftarrow njK}(E)$ describe the amplitudes of transition probabilities between the sets of quantum numbers (njK) and $(n'j'K')$ correspondingly in the (in) and (out) channels at fixed total energy E and will be called reactive S-matrix elements.

APPENDIX E: SOLUTION OF CLASSICAL OSCILLATOR PROBLEM

Now we turn to investigation of equation (51) with natural boundary conditions (53). This equation can be solved with the help of hypergeometric functions. The solution of Eq. (51), which has the form of an incident wave with positive frequency $\omega_i > 0$ in the (in) channel (when $u \to -\infty$) for a model frequency (52) may be written in the form (see for example [54]):

$$\sigma_{in}(\tau) = \omega_i^{-1/2} \exp\left\{ i\omega_+\tau + i\frac{\omega_-}{\lambda} \ln[2\cosh(\lambda\tau)] \right\} \times$$
$${}_2F_1\left[1 - i\frac{\omega_-}{\lambda}, \ -i\frac{\omega_-}{\lambda}; \ 1 + i\frac{\omega_i}{\lambda}; \ \frac{1}{2}(1 + \tanh(\lambda\tau)) \right] \underset{\tau \to -\infty}{\sim} \omega_i^{-1/2} \exp\left(i\omega_i\tau\right), \tag{E1}$$

where

$$\omega_\pm = \frac{1}{2}(\omega_f \pm \omega_i), \quad \omega_{i,f} = A_0 \mp A_1. \tag{E2}$$

Now we can write the solution of Eq. (51) which satisfies another asymptotic condition in the (out) channel:

$$\sigma_{out}(\tau) = \omega_f^{-1/2} \exp\left\{ i\omega_+\tau + i\frac{\omega_-}{\lambda} \ln[2\cosh(\lambda\tau)] \right\} \times$$
$${}_2F_1\left[1 - \frac{\omega_-}{\lambda}, \ -i\frac{\omega_-}{\lambda}; \ 1 - i\frac{\omega_f}{\lambda}; \ \frac{1}{2}(1 - \tanh(\lambda\tau)) \right] \underset{\tau \to +\infty}{\sim} \omega_f^{-1/2} \exp\left(i\omega_f\tau\right). \tag{E3}$$

Both these solutions are connected with each other by Bogoliubov [55] linear transformations:

$$\sigma_{in}(\tau) = C_1 \sigma_{out}(\tau) - C_2 \sigma_{out}^*(\tau), \tag{E4}$$

Coefficients C_1 and C_2 are easily calculated, using of properties of hypergeometric functions:

$$C_1 = < \sigma_{in}(\tau)\sigma_{out}(\tau) >_\tau = \left(\frac{\omega_f}{\omega_i}\right)^{1/2} \frac{\Gamma(1 + i\omega_i/\lambda)\Gamma(i\omega_f/\lambda)}{\Gamma(1 + i\omega_+/\lambda)\Gamma(i\omega_-/\lambda)},$$

$$C_2 = - < \sigma_{in}(\tau)\sigma_{out}^*(\tau) >_\tau = \left(\frac{\omega_f}{\omega_i}\right)^{1/2} \frac{\Gamma(1 + i\omega_i/\lambda)\Gamma(-i\omega_f/\lambda)}{\Gamma(1 - i\omega_+/\lambda)\Gamma(-i\omega_-/\lambda)}. \tag{E5}$$

Recall that similar to (E4), the following expression may be written for the solution $\sigma_{out}(\tau)$:

$$\sigma_{out}(\tau) = C_1 \sigma_{in}(\tau) - C_2 \sigma_{in}^*(\tau), \tag{E6}$$

Now taking into account (E4), (E5) and (E6) for coefficient C_1 and C_2 we obtain:

$$|C_1|^2 = \frac{\sinh^2(\pi\omega_+/\lambda)}{\sinh(\pi\omega_{in})\sinh(\pi\omega_{out})}, \quad |C_2|^2 = \frac{\sinh^2(\pi\omega_-/\lambda)}{\sinh(\pi\omega_{in})\sinh(\pi\omega_{out})}. \tag{E7}$$

Finally from (E7) we can find the normalization expression:

$$|C_1|^2 - |C_2|^2 = 1. \tag{E8}$$

So, taking into account (E3) and (E7), we get the exact solution of Eq. (51), which we must use for future analytical computations, in the form (E4).

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